A Diffusion Equation for Quantum Adiabatic Systems

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Abstract

For ergodic adiabatic quantum systems, we study the evolution of energy distribution as the system evolves in time. Starting from the von Neumann equation for the density operator, we obtain the quantum analogue of the Smoluchowski equation on coarse-graining over the energy spectrum. This result brings out the precise notion of quantum diffusion.

There are many physical situations where a separation of time scales occurs, the adiabatic approximation to an evolution is one of the expressions of such a separation [1]. Classically, an important problem in this context is to describe the evolution in phase space of an ensemble of systems under an ergodic adiabatic Hamiltonian [2]. An ergodic adiabatic Hamiltonian can be defined as one which describes ergodic (usually specialized to chaotic) dynamics under a slowly time-dependent Hamiltonian. In this paper, we study the quantal version of this treatment and obtain results which, in an appropriate limit, reduce to results in [2]. The reasons to present quantum analogue of the classical case study are many-folded. Firstly, classical physics being a special case of quantum physics, it is interesting to know what is the equation that one gets so that the limiting situation is clearly interpreted. Secondly, multiple time-scale analysis is usually employed on classical equations and it is, therefore, interesting to expose how this method may be shown to be fruitful for quantal equations also [3]. Thirdly, a clear analysis based on time-scale separation of the von Neumann equation paves way for the next-order complication that arises in combining the adiabatic and semi-classical limits [4]. The motivation behind this combination of singular limits is provided by a work where first-order velocity-dependent corrections to the lowest adiabatic approximation for the reaction force on the slow system are studied [5]. In the classical setting, one recovers geometric magnetism and deterministic friction as the reaction forces whereas in the half-classical setting (fast system treated quantum mechanically) there is only geometric magnetism, no friction. Deterministic frictional force was found in [6] and is non-zero when the fast motion is classical and chaotic.

Very interesting examples can be cited from different fields of physics and chemistry that resonate with the abovementioned problem. One of the well-studied problem is when there are many particles moving in a time-dependent shape of the box [7]. This is an idealization of nuclear fission and fusion. It has been shown in a numerical experiment that the transition from ordered to chaotic nucleonic motions is accompanied by a transition in collective properties of nuclei from those of elastic solid to visco-elastic to viscous fluid [8]. Quantum mechanical origin of dissipation in finite Fermi systems has been recently explained [9]. It has been found that the geometric phase, γ acquired by a single-particle wavefunction in adiabatic perturbation is related to the absorptive part of the frequency-dependent response function, χ'' of the finite bulk, hence dissipation - we call them $\gamma - \chi$ relations. Mesoscopic

systems can also show this kind of behaviour in their conductivity properties.

We now describe the basic problem. Consider a quantum system evolving adiabatically in time. Since the evolution is adiabatic, we have energy levels at every instant of time and an instantaneous basis. Let us now assume that the energy levels do not cross and the reason for this be left unspecified. In particular, this may arise in a random matrix hypothesis for the system. During the evolution, although the levels do not cross, they may come arbitrarily close to each other. Very small spacing between levels then leads to an increased probability of non-adiabatic Landau-Zener transitions [10] which eventually change the energy distribution of the system. The basic idea behind using the Landau-Zener transitions goes back [11] in the literature of nuclear physics where it is used to explain damping of collective modes.

The classical version of the problem treated here has a distinguished history. Starting from the earlier works of Ehrenfest, in classical context, it was shown first by Lenard [12] that if Hamiltonian, H =constant for $t < 0$ and $t > t_1$, then the values of the reduced action $\oint\ pdq$ for $t < 0$ and $t > t_1$ differ from each other by $\mathcal{O}(\epsilon^m)$, however large m may be. Generality of the adiabatic invariant led Ott [13] to show that the error in ergodic adiabatic invariant in the classical version of our problem is diffusive, however the equation differed from the Smoluchowski equation. The problem was re-examined by Jarzynski [2] where the Smoluchowski equation was restored (although the authors of [13, 2] call it by the name of the Fokker-Planck equation). The quantum version is the subject here. To start with, due to important differences between classical and quantum mechanics, and with lack of a precise notion of chaos in quantum systems [14], it is not clear what will the final equation for energy distribution be. We now show that the equation is different from the classical case.

To begin the analysis, let us consider the Hamiltonian,

$$\hat{H}(t) = \hat{H}_0 + \epsilon t\ \hat{V} \tag{1}$$

where $\hat{H}_0, \hat{V}$ are linear operators. We assume that the evolution in time is adiabatic which corresponds to the smallness of ϵ. As a concrete realization where avoided level crossings may occur, one may assume that the linear operators $\hat{H}_0$ and $\hat{V}$ belong to some random matrix ensembles invariant under a canonical group where it may be mentioned that a detailed study on time correlation functions already exists [15]. Thence, at any instant, system admits an eigenvalue spectrum given by the eigenvalue problem for the

"frozen" Hamiltonian,

$$\hat{H}(\epsilon t)|n(\epsilon t)\rangle = E_n(\epsilon t)|n(\epsilon t)\rangle. \tag{2}$$

The probability of the system residing in the state $|n(\epsilon t)\rangle$ at time t is given in terms of the density operator, $\hat{\rho}$,

$$p_n(t) = \langle n(\epsilon t)|\hat{\rho}|n(\epsilon t)\rangle, \tag{3}$$

with

$$\sum_n p_n(t) = 1 \ \ \forall\ t. \tag{4}$$

On the other hand, the probability of finding the system in the range ΔE about energy E, is defined through

$$p(E)dE = \sum_{E \le E_n \le E+\Delta E} p_n(t) \tag{5}$$

with

$$\int_{-\infty}^{\infty} dEp(E) = 1. \tag{6}$$

To relate p_n and $p(E)$, let us define the density of states,

$$\Sigma(E) = \frac{\Delta N}{\Delta E} \tag{7}$$

so that

$$p(E)\Delta E = p(E)\frac{\Delta N}{n(E)} = p(N)\Delta N \tag{8}$$

implying thereby

$$p(E) = \Sigma(E)p(N). \tag{9}$$

Eq. (9) relates the probability of finding N levels in the energy range $[E, E+\Delta E]$ and the probability of finding the system in the state corresponding to energy E.

From time $t = 0$,the levels evolve in time, the resulting density operator, $\hat{\rho}$ satisfies

$$i\hbar\frac{\partial\hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}]. \tag{10}$$

Starting from (10), our objective is to derive an equation for the energy distribution,

$$\eta(E) = \int^{E} dE' \mathrm{tr}\{\delta(E' - \hat{H})\hat{\rho}\}. \qquad (11)$$

Since ϵ in (1) is small (adiabaticity) parameter, we have two time-scales - t ("fast" scale) and ϵt ("slow" scale). To incorporate these scales in the problem, we employ the multiple time-scale method for treating the partial differential equation (10). Accordingly, denoting the set of instantaneous states by $\{|n(\epsilon t)\rangle\}$, we can write an expansion for the density operator,

$$\hat{\rho}(\{|n(\epsilon t)\rangle\}, t) = \hat{\rho}_0(\{|n(\epsilon t)\rangle\}, \epsilon t) + \epsilon\hat{\rho}_1(\{|n(\epsilon t)\rangle\}, t, \epsilon t) + ... \qquad (12)$$

with the initial conditions,

$$\hat{\rho}_0 = \hat{\rho}_{00}(\hat{H}(\epsilon t)),\ \hat{\rho}_1 = \hat{\rho}_2 = \hat{\rho}_3 = ... = 0. \qquad (13)$$

Substituting (12) in (10), we get a system of equations separated by different orders of ϵ :

$$\begin{aligned} [\hat{\rho}_0, \hat{H}(\epsilon t)] &= 0, & (14)\\ i\hbar\frac{\partial\hat{\rho}_j}{\partial t} + [\hat{\rho}_j, \hat{H}(\epsilon t)] &= -i\hbar\frac{\partial\hat{\rho}_{j-1}}{\partial\epsilon t}, \quad j = 1, 2, ... & (15) \end{aligned}$$

If there are no other constants of the motion than $H(\epsilon t)$ on the fast scale, or under the Thomas-Fermi approximation, by (14),

$$\hat{\rho}_0(\{|n(\epsilon t)\rangle\}, \epsilon t) = \hat{\rho}_0'(H(\epsilon t), \epsilon t) \qquad (16)$$

where the arbitrariness of $\hat{\rho}_0'$ is removed by insisting that $\hat{\rho}$ remains valid for times $O(\epsilon^{-1})$ by removing secularities in (15) with $j = 1$. To realise this, we operate on the $j = 1$ equation by an arbitrary operator-valued function [16], $g(\hat{H})$ and perform the trace of the resulting equation over the frozen basis,

$$\sum_n \left\langle n\middle|g\frac{\partial\hat{\rho}_1}{\partial t}\middle|n\right\rangle + \frac{1}{i\hbar}\sum_n \langle n|g[\hat{\rho}_1, \hat{H}]|n\rangle = -\sum_n \left\langle n\middle|g\frac{\partial\hat{\rho}_0}{\partial(\epsilon t)}\middle|n\right\rangle. \qquad (17)$$

For $\hat{\rho}_0$ to be valid for times for $O(\epsilon^{-1})$, the right hand side (RHS) of (17) should be set to zero, which leads to

$$\sum_n \left\langle n \middle| g \left[\frac{\partial \rho_0'(\hat{H})}{\partial E} \frac{\partial \hat{H}}{\partial (\epsilon t)} + \frac{\partial \rho_0'(\hat{H})}{\partial (\epsilon t)} \right] \middle| n \right\rangle = 0. \tag{18}$$

Let us now define

$$\begin{aligned} \Sigma(E, \epsilon t) &:= \sum_n \langle n | \delta(E - \hat{H}) | n \rangle \\ &= \frac{\partial}{\partial E} \sum_n \langle n | \Theta(E - \hat{H}) | n \rangle := \frac{\partial \Omega(E, \epsilon t)}{\partial E}; \end{aligned} \tag{19}$$

also, we define an energy average over the "frozen" Hamiltonian by

$$\frac{1}{\Sigma} \sum_n \langle n | \delta(E - \hat{H}) ... | n \rangle := \langle ... \rangle_{E, \epsilon t}, \tag{20}$$

which implies

$$\sum_n \langle n | ... | n \rangle = \int dE \Sigma \langle ... \rangle_{E, \epsilon t}. \tag{21}$$

Now, (18) becomes

$$\Sigma \left(\frac{\partial \hat{\rho}_0'}{\partial E} \left\langle \frac{\partial \hat{H}}{\partial (\epsilon t)} \right\rangle_{E, \epsilon t} + \frac{\partial \hat{\rho}_0'}{\partial (\epsilon t)} \right) = 0. \tag{22}$$

Calling

$$\left\langle \frac{\partial \hat{H}}{\partial (\epsilon t)} \right\rangle_{E, \epsilon t} := u(E, \epsilon t), \tag{23}$$

and using (19), we obtain the identity (see Appendix A),

$$\frac{\partial \Sigma}{\partial (\epsilon t)} + \frac{\partial}{\partial E} (\Sigma u) = 0, \tag{24}$$

which is a new derivation of quantum adiabatic theorem. Therefore, (22) reduces to

$$\frac{\partial}{\partial (\epsilon t)} (\hat{\rho}_0' \Sigma) + \frac{\partial}{\partial E} (u \Sigma \hat{\rho}_0') = 0. \tag{25}$$

Then, for $\hat{\rho}_0$, we have

$$\frac{\partial \hat{\rho}_0}{\partial (\epsilon t)} (\{|n\rangle\}, \epsilon t) = \frac{\partial \hat{\rho}_0'}{\partial E} (H, \epsilon t) \left(\frac{\partial H}{\partial (\epsilon t)} - u \right). \tag{26}$$

With this equation and the initial condition (13), we have completely determined $\hat{\rho}_0$.

The notation ∂_x stands for a partial derivative with respect to x.

We now proceed to determine $\hat{\rho}_1$. The formal solution of (15) with $j = 1$ is

$$\begin{aligned} \hat{\rho}_1(\{|n\rangle\}, t, \epsilon t) &= \hat{\rho}_{1i} + \hat{\rho}_{1h} \\ &= -\int_0^t dt' \frac{\partial \hat{\rho}_0}{\partial(\epsilon t)}(\{|N\rangle\}, \epsilon t) + \hat{\rho}_1'(H(\epsilon t), \epsilon t), \end{aligned} \tag{27}$$

where $|N\rangle = |N\rangle(|n\rangle, t, t', \epsilon t)$ is a state reached at time t' evolving backward the state $|n\rangle$ at a time, t, under $\hat{H}(\epsilon t)$. To determine $\hat{\rho}_1'$, we remove secularities at $O(\epsilon^2)$ by a similar procedure as above, resulting in

$$\frac{\partial}{\partial t} \sum_n \langle n|g\hat{\rho}_2|n\rangle = -\sum_n \left\langle n \middle| g \frac{\partial \hat{\rho}_1}{\partial(\epsilon t)} \middle| n \right\rangle, \tag{28}$$

or, more explicitly,

$$\begin{aligned} &\int dE \frac{\partial}{\partial t} \sum_n \langle n|\delta(E - \hat{H}) g\hat{\rho}_2|n\rangle = -\int dE \sum_n \left\langle n \middle| \delta(E - \hat{H}) g \frac{\partial \hat{\rho}_1}{\partial(\epsilon t)} \middle| n \right\rangle \\ &= \int dE \sum_n \langle n|\delta(E - \hat{H}) g \partial_{\epsilon t} \int^t dt' \partial_{\epsilon t} \hat{\rho}_0(\{|N\rangle\}, \epsilon t)|n\rangle \\ &- \int dE \sum_n \langle n|\delta(E - \hat{H}) g \partial_{\epsilon t} \hat{\rho}_1'|n\rangle := T_1 + T_2. \end{aligned} \tag{29}$$

T_1 and T_2 are the abbreviations of the two terms above that line in (29). Using (26), T_1 can be written as

$$T_1 = \int dE \sum_n \langle n|g\delta(E - \hat{H}) \partial_{\epsilon t} \int_0^t dt' \partial_E \hat{\rho}_0' \left(\partial_{\epsilon t} \hat{H} - u\right) |n\rangle. \tag{30}$$

We now employ the notion of distributional or weak derivative of distributions (denoted by $\delta'(x)$ in the case od delta distributions). Employing the following property of the Dirac delta distributions [17], viz.,

$$\delta(E - \hat{H}) \partial_{\epsilon t} \Phi = \delta'(E - \hat{H}) \partial_{\epsilon t} \hat{H} \Phi, \tag{31}$$

(30) becomes

$$
\begin{aligned}
T_1 &= \int dE \sum_n \langle n|g\delta'(E-\hat{H})\partial_{\epsilon t}\hat{H} \int_0^t dt' \partial_E \hat{\rho}_0' (\partial_{\epsilon t}\hat{H} - u)|n\rangle \\
&= -\int dE \sum_n \langle n|g\delta(E-\hat{H})\partial_E^2 \hat{\rho}_0' \partial_{\epsilon t}\hat{H} \int_0^t dt' (\partial_{\epsilon t}\hat{H} - u)|n\rangle \\
&- \int dE \sum_n \langle n|g\delta(E-\hat{H})\partial_E \hat{\rho}_0' \partial_{\epsilon t}\hat{H} \int_0^t dt' \partial_E (\partial_{\epsilon t}\hat{H} - u)|n\rangle
\end{aligned}
\tag{32}
$$

where use has been made of

$$
\delta'(E-\hat{H})\partial_E \hat{\rho}_0' = -\delta(E-\hat{H})\partial_E^2 \hat{\rho}_0'. \tag{33}
$$

This complicated set of terms can be simplified somewhat. To do so, we rewrite T_1 in a way that will help us in introducing two-time correlation functions later. So,

$$
\begin{aligned}
T_1 &= -\int dE \sum_n \langle n|g\delta(E-\hat{H})\partial_E^2 \hat{\rho}_0' \int_{-t}^0 ds (\partial_{\epsilon t}\hat{H}(\{|n\rangle\}) - u)(\partial_{\epsilon t}\hat{H}(\{|n\rangle\}) - u)|n\rangle \\
&- \int dE \sum_n \langle n|g\delta(E-\hat{H})\partial_E \hat{\rho}_0' \int_{-t}^0 ds (\partial_{\epsilon t}\hat{H}(\{|n\rangle\}) - u)\partial_E (\partial_{\epsilon t}\hat{H}(\{|N\rangle\}) - u)|n\rangle \\
&- \int dE \sum_n \langle n|g\delta(E-\hat{H})\partial_E \hat{\rho}_0' \int_{-t}^0 ds \quad u\partial_E (\partial_{\epsilon t}\hat{H} - u)|n\rangle
\end{aligned}
\tag{34}
$$

The average two-time correlation function can now be introduced :

$$
\begin{aligned}
&C_{\epsilon t}(s,E) = \langle \{\partial_{\epsilon t}\hat{H}(\{|n\rangle\},\epsilon t) - u\}\{\partial_{\epsilon t}\hat{H}(\{|N\rangle\},\epsilon t) - u\}\rangle_{E,\epsilon t} \\
&= \frac{1}{\Sigma}\sum_n \left\langle n|\delta(E-\hat{H})\{\partial_{\epsilon t}\hat{H}(\{|n\rangle\},\epsilon t) - u\}\{\partial_{\epsilon t}\hat{H}(\{|N\rangle\},\epsilon t) - u\}|n\right\rangle
\end{aligned}
\tag{35}
$$

Before getting back to (34), we note some simple relations. First of all, we can write :

$$
\begin{aligned}
&\Sigma\partial_E \int_{-t}^0 ds C(s) \\
&= \Sigma\partial_E \left[\int_{-t}^0 ds \frac{1}{\Sigma}\sum_n \left\langle n|\delta(E-\hat{H})\{\partial_{\epsilon t}\hat{H}(\{|n\rangle\},\epsilon t) - u\}\{\partial_{\epsilon t}\hat{H}(\{|N\rangle\},\epsilon t) - u\}|n\right\rangle\right] \\
&= -\frac{1}{\Sigma}\frac{\partial\Sigma}{\partial E}\int_{-t}^0 ds \sum_n \left\langle n\middle|\delta(E-\hat{H})\{\partial_{\epsilon t}\hat{H}(\{|n\rangle\}) - u\}\{\partial_{\epsilon t}\hat{H}(\{|N\rangle\}) - u\}\middle|n\right\rangle
\end{aligned}
\tag{36}
$$

Secondly,

$$\frac{\partial}{\partial E}\left(\Sigma\int_{-t}^{0} dsC(s)\right) = 0. \tag{37}$$

With (36) and (37), we can now write a relation,

$$\Sigma\frac{\partial^2\hat{\rho}_0'}{\partial E^2}\int_{-t}^{0} dsC(s) = \frac{\partial}{\partial E}\left(\Sigma\frac{\partial\hat{\rho}_0'}{\partial E}\int_{-t}^{0} dsC(s)\right) \tag{38}$$

which we shall use shortly.

To simplify T_1 and T_2, we have to employ some further averaging procedure. We call this a coarse-graining in which we replace a function of an eigenvalue, E_n by some average quantity such that the explicit dependence on the label n disappears. One of the ways it may be done is by an integration over the average density of states. The essential point about averaging is that the spectrum "seen" by the system is a continuous one.

After some tedious manipulations, repeated usage of the properties of distributions [17], and effecting coarse-graining, we arrive at

$$\begin{aligned}
T_1 \quad = \quad & -2\int dE\overline{g}(E)\overline{\partial_E^2\hat{\rho}_{nn}'}\Sigma\int_{-t}^{0} dsC_{\epsilon t}(s,E) \\
- \quad & \int dE\overline{g}(E)\overline{\partial_E\hat{\rho}_{nn}'}\Sigma\partial_E\int_{-t}^{0} dsC_{\epsilon t}(s,E) \\
+ \quad & \int dE\overline{g}(E)\overline{\partial_E\hat{\rho}_{nn}'}\langle n|\delta(E-\hat{H})\partial_E(\partial_{\epsilon t}H(\{|n\rangle\})) - u). \\
& .\int_{-t}^{0} ds(\partial_{\epsilon t}H(\{|N\rangle\})) - u)|n\rangle \\
- \quad & \int dE\overline{g}(E)\overline{\partial_E\hat{\rho}_{nn}'}\ u\ \langle n|\delta(E-\hat{H}) \\
& \partial_E\left[\int_{-t}^{0} ds(\partial_{\epsilon t}H(\{|N\rangle\})) - u)\right]|n\rangle,
\end{aligned} \tag{39}$$

where we have employed *ad hoc* coarse-graining and replaced

$$\begin{aligned}
& g(E_n) \ \text{ by } \ \overline{g}(E), \text{ and} \\
& \left\langle n\left|\frac{\partial^2\hat{\rho}_0'}{\partial E^2}\right|n\right\rangle \ \text{ by } \ \overline{\frac{\partial^2\hat{\rho}_0'}{\partial E^2}}.
\end{aligned} \tag{40}$$

The last two terms are of the same order and opposite sign, so they will simply compensate for each other.

Because, for times of $\mathcal{O}(\frac{1}{\epsilon})$,

$$\int_{-t}^{0} dsC(s) = \frac{1}{2}\int_{-\infty}^{\infty} dsC(s) := \frac{1}{2}G_2, \tag{41}$$

we can write for T_1 :

$$T_1 = -\int dE\overline{g}(E)\frac{\partial}{\partial E}\left[\Sigma\overline{\frac{\partial\hat{\rho}_0'}{\partial E}}G_2\right] - \frac{1}{2}\int dE\overline{g}(E)\Sigma\overline{\frac{\partial\hat{\rho}_0'}{\partial E}}\frac{\partial G_2}{\partial E}. \tag{42}$$

Notice that T_2 has the same form as the expression involving $\hat{\rho}_0'$ in (18), manipulations are identical. Finally, the condition that removes secularities to $\mathcal{O}(\epsilon^2)$ is

$$\frac{\partial}{\partial(\epsilon t)}(\hat{\rho}_1'\Sigma) + \frac{\partial}{\partial E}(u\hat{\rho}_1'\Sigma) - \frac{\partial}{\partial E}\left(\Sigma G_2\overline{\frac{\partial\hat{\rho}_0'}{\partial E}}\right) - \frac{1}{2}\Sigma\overline{\frac{\partial\hat{\rho}_0'}{\partial E}}\frac{\partial G_2}{\partial E} = 0. \tag{43}$$

In terms of occupation probabilities, p_0 and p_1 (Cf. Eq. (3)), we have

$$\frac{\partial}{\partial(\epsilon t)}(p_0\Sigma) + \frac{\partial}{\partial E}(up_0\Sigma) = 0, \tag{44}$$

$$\frac{\partial}{\partial(\epsilon t)}(p_1\Sigma) + \frac{\partial}{\partial E}(up_1\Sigma) - \frac{\partial}{\partial E}\left(\Sigma G_2\frac{\partial p_0}{\partial E}\right) - \frac{1}{2}\Sigma\frac{\partial p_0}{\partial E}\frac{\partial G_2}{\partial E} = 0. \tag{45}$$

The energy distribution, defined as

$$\eta = \Sigma\left\langle\hat{\rho}\right\rangle_{E,\epsilon t} \to \Sigma\left\langle\overline{\hat{\rho}}\right\rangle_{E,\epsilon t}, \tag{46}$$

follows the following equation,

$$\frac{\partial\eta}{\partial t} = -\epsilon\frac{\partial}{\partial E}(u\eta) + \epsilon^2\frac{\partial}{\partial E}\left[G_2\Sigma\frac{\partial}{\partial E}\left(\frac{\eta}{\Sigma}\right)\right] + \frac{\epsilon^2}{2}\Sigma\frac{\partial G_2}{\partial E}\frac{\partial}{\partial E}\left(\frac{\eta}{\Sigma}\right), \tag{47}$$

which is the final result. This equation is different insofar as there is an extra term as compared to the Smoluchowski equation. Thus, the diffusion in quantum systems has to be qualitatively and quantitatively different as the diffusion coefficient will be different from the one we have in the Smoluchowski equation.

It is clear that the difference between (47) and the Smoluchowski equation is the derivative of tegrated time correlation function. This is, indeed,

reminiscent of the relations between friction and diffusion coefficients in weak-turbulence plasma theory [18]. This brings us to the premise on which we began, the time scales.

First of all, the time scale associated with the decay of correlation function,

$$t_c := [C(0)]^{-1} \int_{-\infty}^{+\infty} C(s) ds. \tag{48}$$

If the quantum system considered is modelled as a random matrix of dimension N [15] with large N, we know that correlation function will decay very rapidly. Thus, t_c can be very small if the quantum systems possess the following properties : (a) the number of eigenvalues is very large, and the energy spectrum is complex, and, (b) the corresponding classical system is chaotic. Chaos in the underlying classical system plays a fundamental role in the decay of correlation functions. It was recently shown [19] that the quantum time-depende correlations in a Fermionic system are dominated by the classical correlation function. The decay of the correlation function is shown in this work to be governed by the eigenvalues of the Liouvillian operator. Thus, t_c is related to the Liapunov exponents and other detailed features of chaos. In classical ergodic adiabatic systems, the time t (fast scale) is much larger than t_c, thus the third term of (47) is zero. However, in quantal systems, we have the quantum mechanical scale, $t_q = \hbar/S$ (S being the mean level spacing) which is why the third term at $\mathcal{O}(\epsilon^2)$ is explicitly present. If $t_q \ll t_c \ll t$, the quantum effects will dominate, and all the terms in (47) will be important. If $t_c \ll t_q \ll t$, then the system will behave classically initially and eventually, quantum phenomena will become important; so initial evolution will be Smoluchowski-like and then non-Smoluchowski regime sets in. If, however, $t_c \ll t \ll t_q$, then the evolution will be according to the classical equation. Notice, as $\hbar$ becomes small and the system is classical, t_q will become large, which explains how (47) will reduce to the Smoluchowski equation.

In this paper, we have given a formal proof, which is important for any new equation. It is our belief that examples will help in understanding (47) more. We wish to emphasise that the derivation does not assume anything special about the initial density operator (like, e.g., the Kubo-Martin-Schwinger condition). This generality is very important to note. However, we have employed *ad hoc* coarse-graining which, hopefully, does not destroy the novelty.

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APPENDIX - A

To prove (24), observe that

$$\begin{aligned}
\frac{\partial}{\partial E}(\Sigma u) &= \frac{\partial}{\partial E}\left[\sum_m \langle m|\delta(E-\hat{H})|m\rangle \frac{1}{\Sigma}\sum_n \langle n|\partial_{\epsilon t}\hat{H}\delta(E-\hat{H})|n\rangle\right] \\
&= \frac{\partial}{\partial E}\sum_n \langle n|\partial_{\epsilon t}\hat{H}\delta(E-\hat{H})|n\rangle \\
&= \sum_n \langle n|\partial_{\epsilon t}\hat{H}\delta'(E-\hat{H})|n\rangle \\
&= -\frac{\partial}{\partial(\epsilon t)}\sum_n \langle n|\delta(E-\hat{H})|n\rangle \\
&= -\frac{\partial \Sigma}{\partial(\epsilon t)}. \qquad (49)
\end{aligned}$$

The last equality follows because $\langle n|m\rangle = \delta_{nm}$ implies that

$$\begin{aligned}
&\left(\frac{\partial}{\partial(\epsilon t)}\langle n|\right)\delta(E-\hat{H})|n\rangle + \langle n|\delta(E-\hat{H})\left(\frac{\partial}{\partial(\epsilon t)}|n\rangle\right) \\
&= \langle \dot{n}|\delta(E-\hat{H})|n\rangle + \langle n|\delta(E-\hat{H})|\dot{n}\rangle \\
&= [\langle \dot{n}|n\rangle + \langle n|\dot{n}\rangle]\delta(E-E_n) = 0. \qquad (50)
\end{aligned}$$

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